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ON FALTUNG AND CORRELATION OF FUNCTIONS AND THEIR APPLICATION IN PHYSICAL PROBLEMS

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Abstract

This paper deals with a number of applications of the correlation and faltung functions, their Fourier transforms and their integrals. It is possible to show that various types of distortions produced by a recording instrument do not affect the value of the integral of the quantity recorded. This should be of great interest to designers of recording instruments. The advantage of using the F.T. in compounding probability distribution functions is pointed out with an illustration giving a short derivation of Kluyver's famous distribution for the problem of random walk in two dimensions by using this method. Finally, the relation of the correlation function to the Patterson function of a crystal structure is also pointed out.

1. Introduction

Two types of integrals occur in various problems in physics and probability theory, which may be represented in the following form:

$$\int_{-\infty}^{+\infty} g(x')\, h(x - x')\, dx' = f(x) = g \text{F} h(x) \quad \text{(say)}, \tag{1}$$

$$\int_{-\infty}^{+\infty} g(x')\, h(x + x')\, dx' = c(x) = g \text{C} h(x) \quad \text{(say)}. \tag{2}$$

The former is called the "*Faltung*" (folding) or "convolution" of the functions $g(x)$ and $h(x)$. The latter does not seem to have been recognised as a typical form. However, the term "correla ion func ion" of $g(x)$ and $h(x)$ seems to be appropriate for it, as it is the integral of the product of the value of $g(x)$ at x' and of $h(x)$ with its origin shifted by $-x$ at x'.

Equations (1) and (2) can also be written in another equivalent form, namely

$$g\mathrm{F}h\,(x) = \int_{-\infty}^{+\infty} g\,(x - x')\,h\,(x')\,dx' = h\mathrm{F}g\,(x) \tag{3}$$

$$g\mathrm{C}h\,(x) = \int_{-\infty}^{+\infty} g\,(x' - x)\,h\,(x')\,dx' \neq h\mathrm{C}g\,(x) \tag{4}$$

It is the purpose of this paper to point out some of the properties of these functions and a few types of problems in which they find application.

Analogous to the notation of matrix theory, we may define the following functions related to a given (complex) function $f(x) = a(x) + ib(x)$:

$$\tilde{f}(x)\ [\text{'}f\text{-transpose-}x\text{'}] = f(-x) = a(-x) + ib(-x) \tag{5a}$$

$$f^*(x)\ [\text{'}f\text{-conjugate-}x\text{'}] = [f(x)]^* = a(x) - ib(x) \tag{5b}$$

$$f\dagger(x)\ [\text{'}f\text{-dagger-}x\text{'}] = \tilde{f}^*(x) = a(-x) - ib(-x) \tag{5c}$$

It is clear that

$$\tilde{\tilde{f}}(x) = f^{**}(x) = f\dagger\dagger(x) = f(x) \tag{6}$$

and that the four operations identity, transpose, star and dagger form a group of order four, isomorphous with the group $D_2\ (\equiv C_2 \times C_2)$.

By far the most interesting properties of the faltung and correlation functions are concerned with their integral and Fourier transform (F.T.). We define the F.T. of the function $f(x)$ as

$$\mathrm{F}(\mathrm{X}) = \int_{-\infty}^{+\infty} f(x)\,e^{i2\pi\mathrm{X}x}dx, \tag{7a}$$

with the inverse relation

$$f(x) = \int_{-\infty}^{+\infty} \mathrm{F}(\mathrm{X})\,e^{-i2\pi\mathrm{X}x}d\mathrm{X}. \tag{7b}$$

Then, it follows that the F.T. of $\tilde{f}(x)$, $f^*(x)$ and $f\dagger(x)$ are $\tilde{\mathrm{F}}(\mathrm{X})$, $\mathrm{F}\dagger(\mathrm{X})$ and $\mathrm{F}^*(\mathrm{X})$ respectively and their integrals are F, F^* and F^* respectively, where

$$\mathrm{F} = \mathrm{F}(0) = \int_{-\infty}^{+\infty} f(x)\,dx. \tag{8}$$

Using the above results, the following are readily proved:

$$g\mathrm{C}h = \tilde{g}\mathrm{F}h \tag{9}$$

$$h\mathrm{C}g = \tilde{h}\mathrm{F}g = g\mathrm{F}\tilde{h} = \widetilde{g\mathrm{C}h} \tag{10}$$

$$g\mathrm{F}h^* = (g^*\mathrm{F}h)^* \tag{11}$$

$$g\dagger\mathrm{F}h = g^*\mathrm{C}h = h\mathrm{F}g\dagger \tag{12}$$

In particular, the results shown in Table I are noteworthy. Here, G (X), H (X) are the Fourier transforms of $g(x)$ and $h(x)$ and G and H are their integrals. The results that $\int_{-\infty}^{+\infty} g\mathrm{F}h\,(x)\,dx = \mathrm{GH}$ and $\int_{-\infty}^{+\infty} g\mathrm{C}h\,(x)\,dx = \mathrm{GH}$ may be called the "Faltung integral theorem" and the "correlation integral theorem" respectively.

TABLE I

Fourier transforms and integrals of faltung and correlation functions

Correlation function	Equivalent expression as a faltung	Fourier transform	Integral
$\tilde{g}\mathrm{C}h$	$g\mathrm{F}h$	G (X) H (X)	GH
$g\mathrm{C}h$	$\tilde{g}\mathrm{F}h$	$\bar{\mathrm{G}}$ (X) H (X)	GH
$g^*\mathrm{C}h$	$g\dagger\mathrm{F}h$	G^* (X) H (X)	G*H
$g\dagger\mathrm{C}h$	$g^*\mathrm{F}h$	G† (X) H (X)	G*H

The extension of these equations to higher dimensions can readily be made with the following definitions:

$$g\mathrm{F}h\,(\mathbf{r}) = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} g(\mathbf{r}')\,h(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}' \tag{13}$$

$$g\mathrm{C}h\,(\mathbf{r}) = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} g(\mathbf{r}')\,h(\mathbf{r}+\mathbf{r}')\,d\mathbf{r}'. \tag{14}$$

The Fourier transform is

$$\mathrm{F}(\mathbf{R}) = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} f(\mathbf{r})\,e^{i2\pi\mathbf{R}\cdot\mathbf{r}}\,d\mathbf{r} \tag{15}$$

with the inverse

$$f(\boldsymbol{r}) = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \mathrm{F}(\mathbf{R})\, e^{-i2\pi \mathbf{R}.\boldsymbol{r}} d\mathbf{R}. \tag{16}$$

All the results mentioned above are then valid if x is replaced by $\boldsymbol{r}$ and X by $\mathbf{R}$.

So also, the concept of the faltung function can be extended to the faltung or convolution of any number of functions $g_1, g_2, \ldots g_k$. Writing the integral defining the faltung of $g_1(\boldsymbol{r})$ and $g_2(\boldsymbol{r})$ in the symmetrical form

$$g_1 \mathrm{F} g_2(\boldsymbol{r}) = \int_{-\infty}^{+\infty} g_1(\boldsymbol{r}_1)\, g_2(\boldsymbol{r}_2)\, d\boldsymbol{r}_1, \quad \boldsymbol{r}_1 + \boldsymbol{r}_2 = \boldsymbol{r}, \tag{17}$$

we have more generally

$$\begin{aligned} f(\boldsymbol{r}) &= g_1 \mathrm{F} g_2 \mathrm{F} \ldots \mathrm{F} g_k(\boldsymbol{r}) \\ &= \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} g_1(\boldsymbol{r}_1)\, g_2(\boldsymbol{r}_2) \ldots g_k(\boldsymbol{r}_k)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 \ldots d\boldsymbol{r}_{k-1}, \end{aligned}$$

with

$$\boldsymbol{r}_1 + \boldsymbol{r}_2 + \ldots + \boldsymbol{r}_k = \boldsymbol{r}. \tag{18}$$

It is then readily shown that

$$\mathrm{F}(\mathbf{R}) = \mathrm{G}_1(\mathbf{R})\, \mathrm{G}_2(\mathbf{R}) \ldots \mathrm{G}_k(\mathbf{R}), \tag{19}$$

or *the F.T. of the faltung function is the product of the F.T.'s of the* k *individual functions.*

We shall now consider the application of these functions to a variety of problems which occur in physics. These have been chosen with the idea of illustrating the types of such problems and no attempt is made to make them exhaustive.

2. MICROPHOTOMETER RECORD

Suppose we are scanning a series of lines on a photographic plate by means of a microphotometer, whose exploring beam has a finite width w (say). For convenience, let the plate be a positive print of a spectrum, so that $h(x)$ [Fig. 1 (*a*)] represents the true variations in the transmission. However, because of the finite width of the microphotometer spot, the record $\phi(x)$ [Fig. 1 (*b*)] will not be equally sharp. It is readily seen that $\phi(x)$ is the correlation function of g with h, *i.e.*,

$$\phi(x) = \int_{-\infty}^{+\infty} g(x')\, h(x + x')\, dx = g \mathrm{C} h(x). \tag{1}$$

The interesting point is that the application of the correlation integral theorem gives

$$\int_{-\infty}^{+\infty} \phi(x)\,dx = \int_{-\infty}^{+\infty} g(x)\,dx \;.\; \int_{-\infty}^{+\infty} h(x)\,dx \tag{2}$$

or Area under the curve in the record = w (area under the true curve) (3)

where w = width of the microphotometer beam [the intensity being scaled such that $g(x) = 1$ within this width]. Thus, in spite of the distortion in the shape of the lines, the *integrated value* obtained from the record is proportional to the correct value. In fact, from the correlation integral theorem, this is true even if the intensity distribution in the microphotometer spot is not uniform. Extending this idea to the individual lines in the record [Fig. 1 (*b*)]. the *areas* under the different peaks would be exactly proportional to the *areas* under the corresponding peaks in Fig. 1 (*a*), even for an arbitrary shape of the function $g(x)$. Of course, the peaks should be resolved, so that effectively the area is the integral from $-\infty$ to $+\infty$.

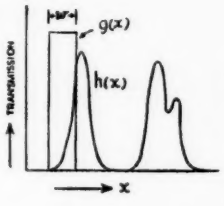

FIG. 1 (*a*)

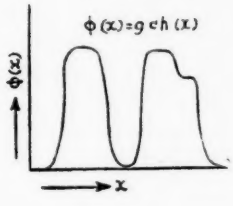

FIG. 1 (*b*)

This result appears to the author to be important, for it is applicable to a variety of other cases, *e.g.*, in recording spectrophotometers and so on. It is obvious that if $h(x) = 1$ for all x, then $\phi(x) = \int g(x)\,dx =$ a constant K for all x. Then, Equation (2) becomes

$$\int_{-\infty}^{+\infty} \phi(x)\,dx = \mathrm{K} \int_{-\infty}^{+\infty} h(x)\,dx. \tag{4}$$

Consequently, if the instrument is graduated to read unity for unit incident intensity when it is uniform, then the constant K becomes effectively unity, and thereafter all integrated values on the record will be correctly scaled automatically.

3. X-RAY REFLECTION WITH DIVERGENT BEAM

A problem which is mathematically very similar to the above is the shape (or angular distribution of intensity) of an X-ray reflection by a crystal, when the incident beam is not perfectly collimated.

Suppose $g(\theta)$ is the distribution of intensity about a mean position θ_0 when the incident beam has zero angular width [Fig. 2 (*a*)]. If $h(\theta'')$ is the angular distribution of intensity in the incident beam [Fig. 2 *b*)], then it is obvious that the reflected intensity $R(\theta)$, when the crystal is set at $\theta_0 + \theta$, is

$$R(\theta) = \int_{-\infty}^{+\infty} g(\theta - \theta'')\, h(\theta'')\, d\theta'' = g \text{F} h(\theta). \tag{5}$$

A little reflection will show why the faltung integral occurs in this case, while the correlation integral occurs in the microphotometer problem. If the functions $f(x)$ and $g(x)$ are symmetrical, the two are one and the same, but they are not so in general.

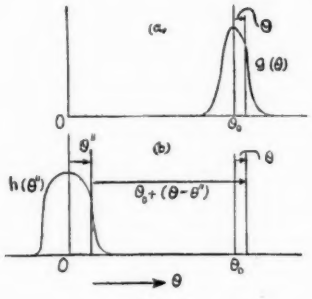

FIG. 2.

Just as in the previous case, an interesting result follows for the integral of $R(\theta)$. By the faltung integral theorem,

$$\int_{-\infty}^{+\infty} R(\theta)\, d\theta = \int_{-\infty}^{+\infty} g(\theta)\, d\theta \,.\, \int_{-\infty}^{+\infty} h(\theta)\, d\theta = \rho E_0, \tag{6}$$

using a notation commonly used in crystallography.

i.e., $E_0 = \int h(\theta)\, d\theta$ is the total energy in the incident beam and $\rho = \int g(\theta)\, d\theta$ is the area under the curve $g(\theta)$ for perfect collimation, usually called the "integrated reflection". Thus,

$$\rho = \frac{\int R(\theta)\, d\theta}{E_0}, \tag{7}$$

and this is true, independent of the shapes of $h(\theta)$ and $g(\theta)$.

This Equation (7) is widely used by crystallographers and is usually derived for the case corresponding to Fig. 2 (*a*), *i.e.*, for a perfectly collimated incident beam. However, in any experimental set-up, the incident beam has a finite angular width and the same formula is used for this case also. An intuitive justification of this may be given by supposing that the incident beam consists of a series of well-collimated components, for each of which the result (6) holds, so that it holds also for the sum. Going to the limit, Equation (7) follows. However, a rigorous justification for taking ρ to be equal to the ratio of the integrals of the observed reflection curve [R (θ)] to the total energy E_0 in the incident beam is only obtainable from the faltung integral theorem.

Incidentally, this shows that in any X-ray technique, irrespective of the shape of the line profile, the integrated intensity of the reflection is a true measure of the quantity ρ.

4. Integrating Meters

(*i*) *Simple averaging.*—Suppose $h(t)$ is the variation of some quantity say with time t, and suppose that a meter is able to register not this value, but only the mean value over the interval $t - \tau$ to $t + \tau$. This is the simplest type of integrating meter, for it gives a reading $\phi(t)$ proportional to the integral of $h(t)$ from $t - \tau$ to $t + \tau$. This can be written down immediately as a correlation function, by taking,

$$\left.\begin{aligned} g(t) &= \mathrm{K} \quad \text{for} \quad -\tau \leqslant x \leqslant +\tau \\ g(t) &= 0 \quad \text{outside this interval} \end{aligned}\right\} \tag{8}$$

and then

$$\phi(t) = \mathrm{K} \int_{-\infty}^{+\infty} h(t + t')\, g(t')\, dt. \tag{9}$$

As in the previous case, the meter can be made to give the correct value for a steady input by making $\mathrm{K} = 1/2\tau$. In that case, it is seen that if a pulse is fed in, then the integrated value of the output is exactly equal to the integrated value of the input, although the shape of the output is distorted.

(*ii*) *Type of integration met with in counting rate meters.*—Counting rate meters, used for instance with Geiger counters, contain a resistance-capacity tank circuit, to which charge is fed in at a rate proportional to the number of counts registered per second. Let $h(t)$ be this input current, so

that the amount of accumulated charge in time dt' at t is $h(t')\,dt'$. Since the tank circuit has a finite time constant = CR (C = capacity, R = resistance), this charge will leak away exponentially as $e^{-a(t-t')}$, where $a = 1/CR$. Thus, the total charge at time t is

$$\int_{-\infty}^{t} h(t')\, e^{-a(t-t')}\, dt' = f(t) \quad \text{(say)}. \tag{10}$$

This can be put as a faltung function by defining

$$\left.\begin{aligned} g(t) &= e^{-at} \quad \text{for} \quad t \geqslant 0 \\ g(t) &= 0 \quad\;\; \text{for} \quad t < 0 \end{aligned}\right\} \tag{11}$$

when

$$f(t) = g \text{F} h(t) = \int_{-\infty}^{+\infty} h(t')\, g(t - t')\, dt'. \tag{12}$$

The voltage across the condenser is obviously $V(t) = f(t)/C$ and so

$$V(t) = \frac{1}{C}\, g \text{F} h(t). \tag{13}$$

Consequently, if there is a sharp peak in the counting rate, and the true integrated value is $\int h(t)\,dt = H$, then the integral of the record, which is the voltage, is

$$\int V(t)\,dt = \frac{1}{C}\int g \text{F} h(t)\,dt = \frac{1}{C}\int g(t)\,dt \,.\, \int h(t)\,dt$$

$$= \frac{H}{C}\int_{0}^{\infty} e^{-at}dt = \frac{H}{Ca} = HR. \tag{14}$$

Thus, the integral of the recorded trace is exactly proportional to the integral of the input (H), the constant of proportionality being R. Once again, we find that the distortion of the shape of the peak does not matter and that the total area under the recorded curve is exactly proportional to the true value.

Incidentally, the absence of the capacity value (C) in HR of Eqn. (14) shows that, once the instrument is correctly calibrated, then the time constant can be altered by changing C, without affecting the calibration.

5. Effect of Delay with or without Integration

It is obvious that a simple delay cannot affect the integrated value of a quantity. Thus, if

$$f(x) = h(x - a).$$

then

$$\int_{-\infty}^{+\infty} f(x)\,dx = \int_{-\infty}^{+\infty} h(x - a)\,dx = \mathrm{H}. \tag{15}$$

On the other hand, suppose there is a delay in recording in addition to integration in an integrating meter. Denoting the independent variable quite generally by x (this may be time or distance on a recording paper), the two effects together can be represented by the equation

$$f(x) = \mathrm{K} \int_{-\infty}^{+\infty} h(x - x' + a)\, g(x')\,dx' = \mathrm{K}g\mathrm{F}h(x + a). \tag{16}$$

It is again clear that the integrated value of $f(x)$ will be proportional to the integrated value of $h(x)$.

These results can be generalised as follows: *Irrespective of any instrumental effects like integrating time, delay, etc., if a meter is calibrated to read correctly for constant input, the integral of the record will be correct even for varying input, i.e.,* there may be a large distortion in the record, but the integrated value will be correct.

6. Probability Distribution Functions

The concept of the faltung of two or more functions occurs most frequently in the applications of probability theory. If $p_1(x_1)$, $p_2(x_2)$, ... $p_n(x_n)$ are the probability distribution functions* (p.d.f.) of a number of random variables x_i and if $x = \sum_1^n x_i$ and the variables are independent, then the p.d.f. of x is clearly

$$p(x) = \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} p_1(x_1)\, p_2(x_2) \dots p_n(x_n)\,dx_1 \dots dx_{n-1} \tag{17}$$

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* The term distribution function is used here to denote the function $p(x)$, which gives the probability that the variable lies between x and $x + dx$ as $p(x)\,dx$. This agrees with the nomenclature in physics and applied mathematics (*e.g.*, Maxwell distribution of velocities, Gaussian distribution of errors, etc.), besides being description of the actual function. It is a pity that in the more abstract studies on probability, the term "distribution" is used for the integral of this function, while the term "frequency function" is used for $p(x)$.

with

$$x = x_1 + x_2 + \ldots + x_n. \tag{18}$$

Thus, $p(x)$ is the faltung of the n functions $p_i(x_i)$.

Proof that p (x) *is a p.d.f.*—Mathematically, a p.d.f. $p_i(x_i)$ satisfies the following two conditions

$$\left.\begin{aligned} &(a)\ p_i(x_i) \text{ is positive for all } x_i \\ &(b)\ \int_{-\infty}^{+\infty} p_i(x_i)\, dx_i = 1 \end{aligned}\right\}. \tag{19}$$

The range of integration may be finite in many cases, but it can always be made infinite by putting $p_i = 0$ outside this range.

Now Equation (17) may be derived by probability arguments and $p(x)\,dx$ then gives the probability that the compounded variable x lies between x and $x + dx$. However, the simplest proof that the function $p(x)$ defined by Equation (17) is in fact a p.d.f. and satisfies 19 (a) and (b) is obtained by an application of the faltung integral theorem. Then it follows that

$$\int_{-\infty}^{+\infty} p(x)\, dx = \prod_{i=1}^{n} \int_{-\infty}^{+\infty} p_i(x_i)\, dx_i = 1, \tag{20}$$

thus proving the condition 19 (a). The positivity condition (19 b) is obtained from the fact that all the terms occurring in Equation (17) are positive.

Now it immediately follows from Equations (17) and (18) that their F.T.'s are related by the equation

$$\mathrm{P}(\mathrm{X}) = \mathrm{P}_1(\mathrm{X})\ \ldots\ \mathrm{P}_n(\mathrm{X}) = \prod_{i=1}^{n} \mathrm{P}_i(\mathrm{X}). \tag{21}$$

In stochastic theory, $P(x)$ is called the characteristic function of $p(x)$ and Equation (19) may be then interpreted in the following form: "When a number of p.d.f.'s are compounded, the characteristic function of the compounded p.d.f. is the product of the charact ristic functions of the individual ones."

The above results are readily extended to joint probability distributions in any number of variables.

Thus, if

$$\boldsymbol{r} = \boldsymbol{r}_1 + \boldsymbol{r}_2 + \ldots + \boldsymbol{r}_n,$$

then

$$p(\boldsymbol{r}) = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} p_1(\boldsymbol{r}_1) \cdots p_n(\boldsymbol{r}_n)\, d\boldsymbol{r}_1 \cdots d\boldsymbol{r}_{n-1} \tag{22}$$

and we have also

$$p(\boldsymbol{r}) = \int \prod_{i=1}^{n} \mathrm{P}_i(\mathbf{R})\, e^{-i2\pi \boldsymbol{r}\cdot\mathbf{R}} d\mathbf{R} \tag{23}$$

where

$$\mathrm{P}_i(\mathbf{R}) = \int p_i(\boldsymbol{r}_i)\, e^{i2\pi \boldsymbol{r}_i\cdot\mathbf{R}} d\boldsymbol{r}_i. \tag{24}$$

In fact, the F.T. is a convenient means of doing the compounding, either numerically or even theoretically. Thus, Equations (23) and (24) are directly applicable to the derivation of the distribution $\phi_n(\boldsymbol{r})\, d\boldsymbol{r}$ for the position of a particle after it has suffered n random displacements, when the distribution function for each displacement is given (Theory of Random Flights, Chandrasekhar, 1943). Remembering that 2π is included in the exponent in our formulæ, the above equations give at once Equations (51) and (52) of Chandrasekhar's formulation. Chandrasekhar has in fact used the F.T. method to work out various results in the theory of random flights in three dimensions.

It can also be used to work out in a straight-forward manner the general formula for the problem of random walk in two dimensions. Suppose the i-th step is of length l_i. The problem is to find the probability $W_n(r)\, dr$ that one is at a distance between r and $r + dr$ from the origin after taking n steps in random directions. The function $p_i(\boldsymbol{r}_i)$ is then given by

$$p_i(\boldsymbol{r}_i) = \frac{1}{2\pi}\, \delta(|\, \boldsymbol{r}_i\,|^2 - l_i^2) \tag{25}$$

whose F.T. is just

$$\mathrm{P}_i(\mathbf{R}) = \mathrm{J}_0(2\pi \mathrm{R} l_i).$$

Hence, if $\phi_n(\boldsymbol{r})\, d\boldsymbol{r}$ is the probability that the resultant displacement after n steps lies in an area $d\boldsymbol{r}$ at $\boldsymbol{r}$, then

$$\text{F.T. of } \phi_n(\boldsymbol{r}) = \prod_{i=1}^{n} \mathrm{P}_i(\mathbf{R}) = \prod_{i=1}^{n} \mathrm{J}_0(2\pi \mathrm{R} l_i), \tag{26}$$

so that

$$W_n(r) = 2\pi r \phi_n(r)$$

$$= 2\pi r \int_0^\infty \int_0^{2\pi} e^{-i2\pi R r \cos\phi} \prod_{i=1}^{n} J_0(2\pi R l_i)\, R\,dR\,d\phi$$

$$= 4\pi^2 r \int_0^\infty R J_0(2\pi R r) \prod_{i=1}^{n} J_0(2\pi R l_i)\, dR. \tag{27}$$

Putting $2\pi R = x$, this gives

$$W_n(r) = r \int_0^\infty x J_0(rx) \prod_{i=1}^{n} J_0(l_i x)\, dx, \tag{28}$$

which is identical with the well-known formula of Kluyver (1906) in the form given by Rayleigh (1919), usually obtained by a long derivation.

Fourier transform methods seem to be ideally suited not only for compounding distribution functions, but also for deconvoluting functions,* *e.g.*, to get $h(x)$ from $g \digamma h(x)$ when $g(x)$ is known. The method can be employed for numerical calculations with ease, since routine methods of calculating Fourier transforms are available and the latter have only to be multiplied or divided thereafter.

7. Correlation Function of Real Functions

For a real function $f(x)$, $\tilde{F}(X) = F^*(X)$ and it follows that if both $g(x)$ and $h(x)$ are real functions, then

$$\text{F.T. of } g \subset h(x) = G^*(X)\, H(X).$$

In particular, if g and h are the same function, the function $g \subset g(x)$ may be called the "autocorrelation function" of g. Its Fourier transform is then equal to $G^*(X)\, G(X) = |G(X)|^2$. This function is of very great importance in X-ray crystallography and is known as the Patterson function [$P(x)$] in that field. In fact, the properties of $P(x)$, which is the inverse Fourier transform of $|G(X)|^2$ and of $f(x)$ the faltung which is the inverse Fourier transform of $G(X)\, H(X)$ have been extensively studied in connection with a study of crystal structures by Ramachandran and Raman (1959) and Raman (1959).

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* The use of the F.T. for deconvoluting a function has been pointed out by Stokes (1948, 1955) in connection with the study of X-ray line profiles.

So also, the faltung and Patterson functions and their Fourier transforms have been used by Hosemann and Bagchi (1952) in their formulation of a general theory of diffraction by crystals.

Another field in which this autocorrelation function finds application is in the theory of stationary time series and of coherence phenomena. The results worked out in these fields are capable of generalisation in terms of our notation and results, but these are reserved for a separate paper.

I wish to express my thanks to Dr. P. M. Mathews and Dr. R. Srinivasan for the discussions I had with them during the preparation of this paper.

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MICELLAR SIZE AND SHAPE IN SOLUTIONS OF CALCIUM STEARATE IN CETANE FROM OPTICAL DEPOLARIZATION DATA

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Introduction

The object of this work was to obtain further understanding of the effect of small additions of water to calcium stearate-cetane systems at elevated temperatures, particularly on the micellar size and shape, and the relation between this and the viscosity of the solution and the stability of the grease prepared from it on cooling. Light scattering offers a powerful method for the study of such factors and for their variation with temperature and concentration of water or other additives in the system (Stacy, 1956). In the present work measurements were made over a temperature range of the depolarization factors of the transversely scattered light from 1% and 18% solutions of calcium stearate containing variable amounts of water. Although this method can give only a qualitative indication of relative changes in size, shape or anisotropy, it has the advantage of direct applicability at the high temperatures involved with the present systems and can be used with concentrated systems provided, as in the present work, errors arising from secondary scattering and convergence of the incident light are avoided. Unambiguous interpretation, however, may be impossible unless the intrinsic anisotropy is independently determined. In the case of concentrated systems, where the main observed effects may be due to inter-particle interactions, attempted interpretation in terms of dilute solution theory and the size, anisometry and anisotropy of the individual scattering units may be quite fallacious. Quantitative conclusions require independent determination of the intensities of the individual components of the scattered light over a wide range of angles and at a series of concentrations, data which are usually not available.

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Experimental

Materials.—The anhydrous calcium stearate used in these experiments was prepared according to the method of Vold, Hattiangdi and Vold (1949) and was shown to be a similar product by its X-ray diffraction pattern. The cetane used (Humphrey Wilkinson Company, Connecticut) had a refractive index $n_{20}^{o} = 1{\cdot}4350$, and was centrifuged before use in a Servall high speed centrifuge at 13,000 r.p.m. to remove suspended impurities.

Preparation of Samples.—Three gram samples of calcium stearate, cetane and water in the requisite amounts were sealed in evacuated pyrex-glass tubes having an internal diameter of 1·5 cm. and wall thickness of 0·6 mm., heated to fluidity, thoroughly mixed, and equilibrated at the desired temperature for an hour before measurements were made. Visual observations between crossed polaroids showed that the solutions obtained were homogeneous and istoropic in the temperature range studied, *viz.*, 130–200° C.

Measurement of Depolarization Factors.—The sealed tubes were placed at the centre of a well-lagged, electrically heated, cylindrical chamber, the temperature of which was controlled with an accuracy of $\pm$ 1·5° C. by varying the voltage applied to the heater. The chamber was provided with suitable apertures for the incident, transmitted and scattered beams.

The optical arrangement and techniques used were the same as those employed by Krishnan (1934, 1935), the depolarization factors being measured visually in the horizontal transverse direction ($\theta = 90°$) by the Cornu method. The depolarization values were reproducible to within $\pm$ 2% of the measured values in the 1% solutions and to $\pm$ 4% in the 18% systems. The light source was an Ediswan 500 c.p. pointolite lamp from which a narrow band of wavelengths in the region of 5500 Å was isolated by a suitable green filter. The solutions studied were free from fluorescence. Errors due to convergence and secondary scattering were minimized by using a very thin, nearly parallel incident beam (2 mm. high and 0·25 mm. thick) (Stacy, 1956, p. 69). For the same reason the diameter of the sample tube (1·5 cm.) was chosen such that it was large enough to avoid parasitic reflections, etc., while at the same time the distance traversed by the scattered light before emerging from the cell is small. Since the incident beam was very thin and so adjusted as to be precisely along a diameter of the circular section of the tube, it was possible to make the depolarization measurements by matching the intensities of the two tracks with the analyzing double-image prism-Nicol combination in the exact transverse horizontal direction.

The depolarization factors ρ_u, ρ_v and ρ_h refer respectively to the depolarization of the scattered light when the incident beam is unpolarized, polarized

with the electric vector vertical, and with the electric vector horizontal. The existence of a relation between these was first shown by Krishnan (1934) and has subsequently been proved in a more general way by Perrin (1942) for all symmetrical and isotropic media. While the relation $\rho_u = 1 + 1/\rho_h / 1 + 1/\rho_v$ is valid even for concentrated systems as long as the above criteria are satisfied, a rigorous interpretation of the depolarization factors for the higher soap concentrations in terms of the size, shape and anisotropy of the particles is made difficult by intramolecular interference and the possibility of intermolecular or intermicellar interactions (Doty and Kaufman, 1945; Doty, 1948). Nevertheless it has been found (Yudelson and Rabinovitch, 1956) that even concentrated gel-like systems can behave in a manner analogous to that of liquids, although apparently most of the observed depolarization in such cases is due to intermolecular effects rather than to the intrinsic characteristics of the scattering units.

That secondary scattering was unimportant in the present work, a necessary condition, if the results at higher concentrations are to be trusted, is proved by the fact that values of ρ_h calculated by the Krishnan reciprocity relation from the more easily measured values of ρ_u and ρ_v agreed within 2 to 7% of the value with the experimentally determined value of ρ_h with no systematic difference.

Rheological Measurements.—An approximate measure of the viscosity of the system was obtained by equilibrating the sample at each of the several temperatures, measuring with a stop-watch the time required for the solution to flow from the top to the bottom of the sealed tube when the tube was quickly inverted. Although crude, this method has the advantage of measuring the viscosity on the identical system on which the depolarization measurements were made and under the same conditions.

RESULTS AND DISCUSSION

The values of ρ_u, ρ_v and ρ_h for the different systems are shown as a function of temperature in Figs. 1, 2 and 3. Figure 4 shows the flow times at 155° and 190°C. for a standard distance of 10 cm. as a function of the amount of water added to 18% calcium stearate-cetane systems.

Ever since the development of this method (Krishnan, 1934) there has been keen interest in the use of measurements of the depolarization of scattered light to determine the characteristic parameters of the scattering particles, and recognition that this was possible from the values of ρ_v and ρ_h in sufficiently dilute solutions. However, there are many complications involved, including the differing effects of anisometry of shape and optical anisotropy dependent

on the relative size of the particle with respect to the wavelength of the scattered light, and the effects of particle interaction in all except extremely dilute solutions. Before the theory was thoroughly worked out, it was believed that values of ρ_h could be used to determine the size of the scattering particle irrespective of its anisotropy or anisometry (Doty and Kaufman, 1945; Doty, 1948; Doty and Stein, 1948), ρ_h being unity for small particles and decreasing in value as the particle size increased.

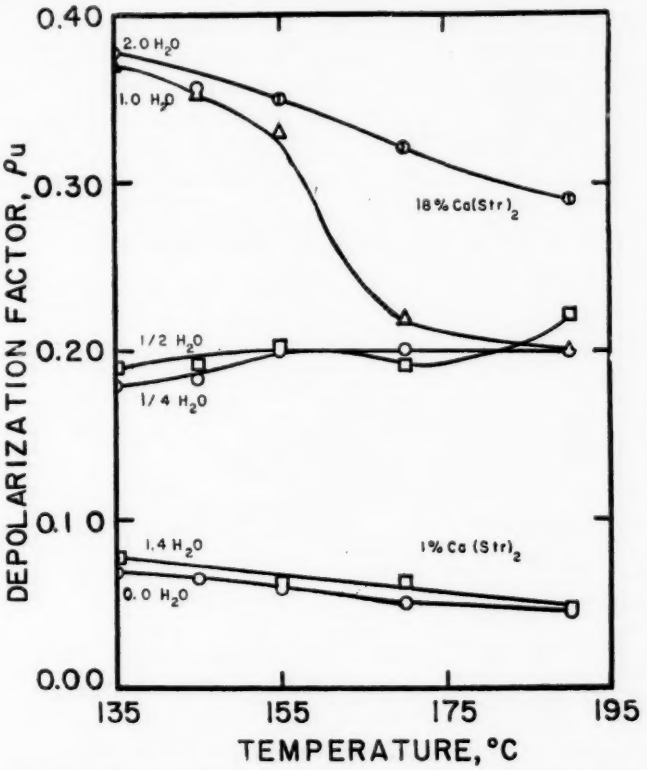

FIG. 1. Depolarization of initially unpolarized light scattered in the transverse horizontal direction by calcium stearate-cetane-water systems.

1% Calcium Stearate: 0, no added water.
□, 1·4 moles H_2O per mole Ca (Str)$_2$

18% Calcium Stearate: 0, ¼ mole H_2O per mole Ca (Str)$_2$
□, ½ mole H_2O per mole Ca (Str)$_2$
△, 1 mole H_2O per mole Ca (Str)$_2$
⊕, 2 moles H_2O per mole Ca (Str)$_2$

It was recognized that the behaviour of ρ_v was more complex, being dependent on both the anisotropy and the anisometry (increasing anisometry may be equated with increasing size) of the particle or molecule, ρ_v being zero for small isotropic particles but increasing to higher values as either anisotropy or anisometry (size) increased. This conclusion was inferred from experimental data for polystyrene (Doty and Kaufman, 1945) and tobacco mosaic virus (Doty and Stein, 1948). Although ρ_v actually was larger rather than smaller for the lower molecular weight polystyrene fraction the increase was then attributed to increased anisotropy rather than decreased size. It is, therefore, evident that no unambiguous information about particle size can be obtained from changes in ρ_v alone, but that independent data on the shape and the anisotropy are also essential. Nevertheless many authors have used the theory in its primitive form relatively uncritically, and possibly mistakenly in some cases, but with considerable success, to determine qualitative changes in particle size or shape in a number of systems (Prasad *et al.*, 1949, 1952; Basu, 1950; Sundaram, 1954; Buch and Sundaram, 1954).

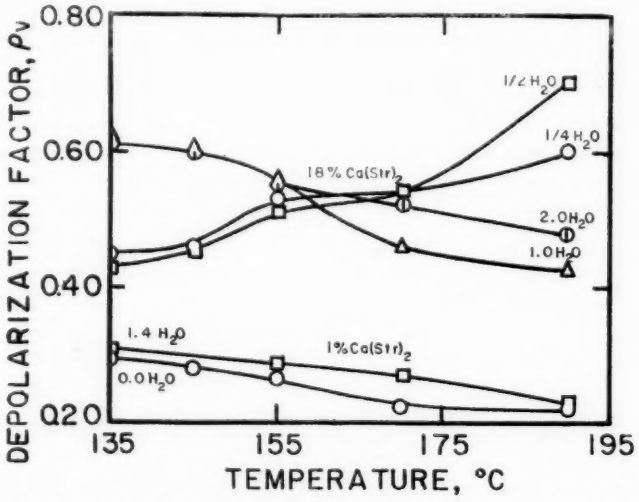

FIG. 2. Depolarization of initially vertically polarized light scattered in the transverse horizontal direction by calcium stearate-cetane-water systems.

1% Calcium Stearate: 0, no added water.
□, 1·4 moles H_2O per mole $Ca(Str)_2$

18% Calcium Stearate: 0, ¼ mole H_2O per mole $Ca(Str)_2$
□, ½ mole H_2O per mole $Ca(Str)_2$
△, 1 mole H_2O per mole $Ca(Str)_2$
⊕, 2 moles H_2O per mole $Ca(Str)_2$

It is now apparent that the situation is more complicated than the earlier investigators realized (Horn, Benoit and Oster, 1951; Horn 1952). The theory has been worked out in detail (Horn, 1955) for molecules small compared to the wavelength of the incident light, for isotropic molecules large compared to the wavelength, and for anisotropic macromolecules treated as rigid rods and as Gaussian coils. Detailed application of this theory to the present data is impossible since it requires knowledge not only of the depolarization ratios but of the intensities, and their variation with angle,

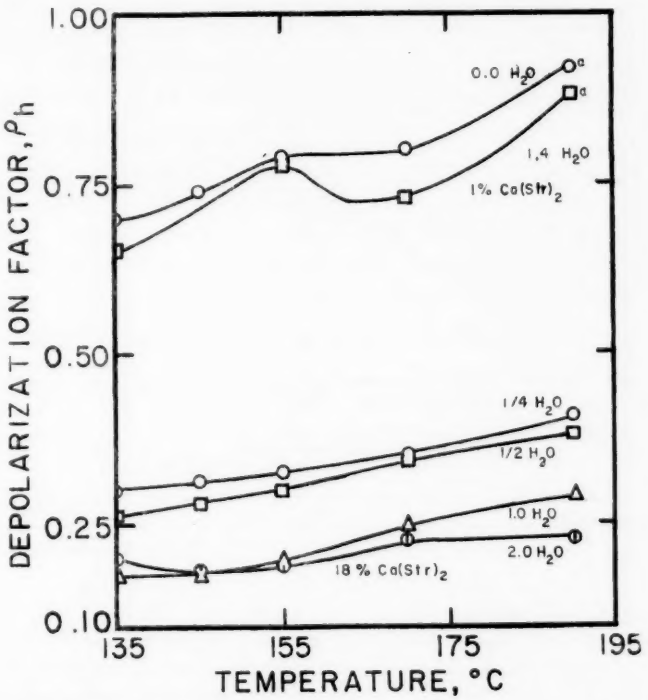

FIG. 3. Depolarization of initially horizontally polarized light scattered in the transverse horizontal direction by calcium stearate-cetane-water systems.

1% Calcium Stearate: 0, no added water.
□, 1·4 moles H_2O per mole Ca (Str)$_2$

18% Calcium Stearate: 0, ¼ mole H_2O per mole Ca (Str)$_2$
□, ½ mole H_2O per mole Ca (Str)$_2$
△, 1 mole H_2O per mole Ca (Str)$_2$
Ⓘ, 2 moles H_2O per mole Ca (Str)$_2$

(*a*) Calculated from ρ_u and ρ_v by the Krishnan relation.

of the individual components involved ($\rho_h = V_h/H_h = H_v/H_h$; $\rho_v = H_v/V_v$, as defined by Doty and Kaufman, 1945), as well as of L/λ, the ratio of the length of the particle to the wavelength of the light, and of the anisotropy, δ, which is determined by the magnitude of the polarizability in different directions through the scattering particle. However, it is easily seen that in the general case if a scattering particle is anisotropic the value of ρ_h is dependent not on size alone but also on the magnitude and sign of the anisotropy.

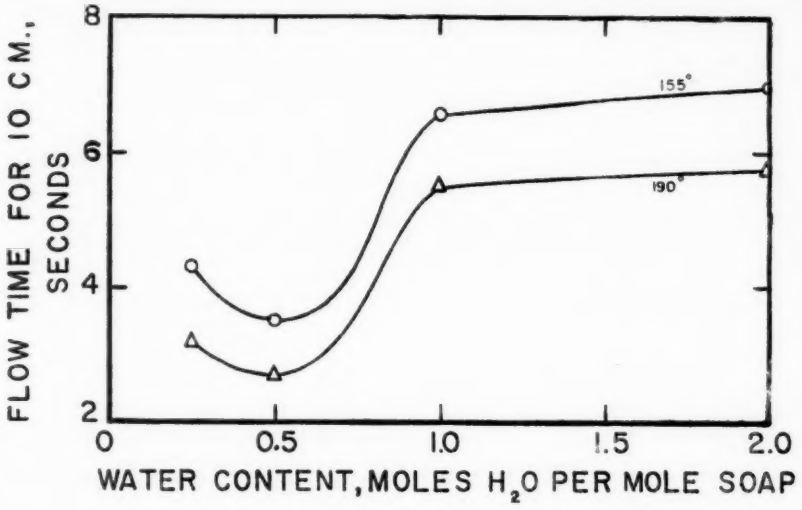

FIG. 4. Flow behaviour of eighteen per cent. calcium stearate systems in cetane with varying water content.

0, values at 155° C.
Δ, values at 190° C.

Horn's calculations (1951, 1955) show that both H_h and V_h decrease as particle size (expressed as L/λ) increases (except for a reversal of the curves for H_h between $L/\lambda = \cdot 6$ and $\cdot 9$ when systems are viewed at angles greater than 90°), the relative rate of decrease of the two depending on the value of the optical anisotropy, δ. Calculation of ρ_h as the ratio of numerical values of H_h and V_h roughly determined from the graphs in Horn's papers shows that if $\delta = 0 \cdot 5$ ρ_h becomes smaller as the particle length increases (L/λ changing from $0 \cdot 3$ to $0 \cdot 9$) whereas at $\delta = 1$ it becomes larger. Hence, unless it is shown that $\delta = 0$ it is not possible to assert unambiguously that particle size has increased because ρ_h has decreased, as has frequently been assumed by previous investigators.

The situation with respect to ρ_v is still more difficult. The earlier workers believed that the value of ρ_v increased from zero toward unity as the size increased. More recently it has been suggested that ρ_v instead decreases as the size increases. Horn's graph (1955, p. 407) shows that at 90° H_v/δ^2 becomes much smaller as L/λ changes from 0·3 to 0·9. Since $\rho_v = H_v/V_v$ this requires that ρ_v must become smaller as the particles become larger, provided δ remains constant and V_v is not greatly dependent on size. As has already been mentioned, the scanty experimental evidence on polystyrene (Doty and Kaufman, 1945) cannot be used to choose between these two alternatives with any certainty. Similarly, the very small value of ρ_v for tobacco mosaic virus solutions (Doty and Stein, 1948) could be attributed either to the very large size of the molecule, or to the fact that it is only slightly anisotropic, since $\rho_v = 0$ when $\delta = 0$.

The present data also consist only of values of the depolarization ratios and their change with temperature and water content, with no information about the anisotropy. Accordingly, it is impossible to reach definitive conclusions as to the changes occurring in micellar size and shape although, with the aid of indirect evidence, reasonable hypotheses can be advanced.

In view of the work of Honig and Singleterry (1954, 1956) on non-aqueous solutions of sodium phenyl stearate it is reasonable to regard the present system as made up of relatively rigid rod-shaped particles with a tendency to form chain like aggregates. The visual transparency suggests that the micelles are not large compared to the wavelength of the light, a supposition supported by the relatively small micellar volumes (corresponding to micellar radii of 82 Å and less) found by Singleterry and co-workers (*loc. cit.*, Kaufman and Singleterry, 1958) in similar systems from fluorescence depolarization measurements. According to Horn (1955) the decrease in V_h ($= H_v$) in systems viewed at 90° is greater as L/λ changes from 0·3 to 0·6 than from 0·6 to 0·9. Since the calcium stearate micelles appear to be relatively small, this suggests that even though they may be anisotropic, it is still justifiable to interpret a decrease in ρ_h from its limiting value of unity as indicative of an increase in particle size, since although both V_h and H_h decrease with increasing particle size, it appears likely that in the range involved V_h decreases the more rapidly.

Examination of the results for 1% systems of calcium stearate in cetane shows that here ρ_h is substantially less than unity, indicative of a rather large micellar size. Moreover, since ρ_h decreases on addition of 1·4 moles water per mole of soap over the whole temperature range, it appears that the added water has increased the size of the scattering particles. This seems surprising

in view of the fact that it has been shown (Honig and Singleterry, 1954; 1956) that initial addition of water to dilute hydrocarbon solutions of alkali and alkaline earth phenyl stearates greatly reduces the viscosity, this effect being attributed to a chain breaking action of the water which should result in a smaller micellar size as well as a decrease in anisometry. However, addition of larger amounts of water resulted in intermicellar aggregation in the case of dilute alkali metal soap solutions as shown by development of viscoelastic behaviour although such an effect was not observed with calcium phenyl stearate. Vold and Coswell (1957) found a close relation between the stability of gels of calcium stearate in cetane and the viscosity of the solutions from which they were prepared, low viscosity solutions with presumably smaller micelles resulting in more stable gels. As the water content increased the rate of liquid loss from the gel (18% soap) decreased up to 1/2 mole water per mole of soap and thereafter increased, while the retention of liquid was maximum at about one mole water per mole of soap. Both these observations suggest that initial addition of water reduces the size of the micelles in the solutions but that increase in its amount to greater than one mole of water per mole of soap causes an increase in micellar size in agreement with the results of the present investigation. This interpretation cannot be accepted without reservation, however, since it is probable that additional water also changes the intrinsic anisotropy because of the likelihood of its being localized in the system rather than homogeneously distributed, and this may effect the direction of change of ρ_h with size.

The increase of ρ_v of 1% systems on addition of water is difficult to interpret since it depends on both anisometry and anisotropy, both of which probably change. Increasing temperature decreases the value of ρ_v which, in this instance, may be due primarily to decrease in anisometry rather than to the anisotropy, since the viscosity presumptively decreases as the temperature increases, which also suggests a shortening of the micelle. Since an increase in temperature will necessarily reduce the tendency toward increased linear extension of the aggregates, this interpretation is also in accord with the decrease in size of micelle with increasing temperature inferred from the increasing values of ρ_h.

Although possible complications due to interaction effects preclude unambiguous interpretation of the results of the depolarization measurements on the concentrated systems, it is still useful to examine the extent to which these are in accord with changes in micellar state inferred from the observed rheological behaviour. For purposes of simplification it is assumed that increasing viscosity may be attributed to increasing size and anisometry of the particles, assuming that solvation and interaction effects remain relatively

constant. On this basis the effect of increasing temperature, which lowers the viscosity of 18% calcium stearate-cetane systems at all water contents, is to reduce the size and anisometry of the micelles. In complete agreement is the fact that ρ_h for all these systems also increases regularly with temperature, indicative of decreasing size of micelle.

The variation of ρ_h with water content may be interpreted in terms of a small increase in micellar size on changing from $\frac{1}{4}$ to $\frac{1}{2}$ mole of water per mole of soap, and a much larger increase in micellar size on passing from $\frac{1}{2}$ to 1 or 2 moles of water per mole of soap. This is in agreement with the viscosity data which suggest that micellar size increases greatly on increasing the water content from $\frac{1}{2}$ to 1 mole of water per mole of soap. However, from the viscosities it would be inferred that the micellar size decreases slightly rather than increasing as water content changes from $\frac{1}{4}$ to $\frac{1}{2}$ mole of water per mole of soap. The discrepancy here may be an indication that in these concentrated systems changes in interaction forces may be more important than changes in the characteristics of the scattering particles.

The variation of ρ_v of 18% systems with temperature and water content is considerably more complicated. The depolarization increases with temperature in the case of water contents of $\frac{1}{4}$ and $\frac{1}{2}$ mole of water per mole of soap and decreases with temperature at water contents of 1 and 2 moles of water per mole of soap. Since the viscosity decreases with increasing temperature in all cases, the size and anisometry may be presumed to decrease. Irrespective of whether size is believed to increase or decrease with increasing ρ_v the behavior changes qualitatively as the water content in the system increases beyond $\frac{1}{2}$ mole per mole of soap, which suggests that either the anisotropy or the molecular interactions must differ at higher and lower amounts of water. Since calcium stearate can form a monohydrate (Vold *et al.*, 1948) it is entirely possible that the variation of anisotropy with temperature may be different at water contents above and below this composition.

Acknowledgment

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Summary

Observations at a series of temperatures of the changes in viscosities and depolarization factors of 1% and 18% solutions of calcium stearate in

cetane to which varying amounts of water have been added can be interpreted in terms of the existence of anisometric micelles. In general, changes in the size of the micelles inferred from values of ρ_h agree with those deduced from the viscosity data. The correlation between anisometry of micelles from rheological and optical observations is much poorer in the case of ρ_v, presumably because of the difficulty in differentiating the contribution of anisometry and anisotropy to ρ_v.

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3-ACETYL-4-HYDROXYCOUMARIN AS A REAGENT FOR THE GRAVIMETRIC DETERMINATION OF ZIRCONIUM AND TITANIUM

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Anschütz *et al.*[1] reported the formation of ammonium, sodium and silver salts of 3-acetyl-4-hydroxycoumarin, and after analysis gave their composition as $NH_4C_{11}H_7O_4$, Na $C_{11}H_7O_4$ and $AgC_{11}H_7O_4$ respectively. Bhat and Jain[2] used this compound as a reagent for the estimation of uranium and thorium, and their separation from each other as well as from cerium (III) and lanthanum. These authors also used it for the spectrophotometric determination of ferrous iron.[3] It has now been found that this reagent precipitates zirconium quantitatively between the pH range 3·5 and 7·0. Titanium also gets precipitated by this reagent over a pH range of 7·0 to 9·0.

When an alcoholic solution of 3-acetyl-4-hydroxycoumarin is added to zirconyl salt solution, a pale yellow precipitate is obtained, which on ignition yields zirconium dioxide. Zirconium can in this way be conveniently determined between the pH 3·5 and 7·0, and under these conditions as little as 2·2 mg. of zirconium dioxide can be estimated.

Titanium is similarly precipitated from a solution of potassium titanyl oxalate with this reagent. The precipitate on ignition gives TiO_2.

Titanium can in this way be estimated between pH 7·0 and 9·0, and under these conditions quantities as low as 7·1 mg. of TiO_2 can be estimated accurately.

Experimental

3-Acetyl-4-hydroxycoumarin was prepared as outlined earlier[2]. 1% ethanol solution of the reagent was employed for estimations.

All other chemicals used were either of A.R. (B.D.H.) quality or E. Merck Pro analysi.

The pH measurements were made with a Beckmann pH meter Model H2 using a glass electrode.

Determination of zirconium with 3-acetyl-4-hydroxycoumarin.—To about 150 ml. of an aqueous solution of Zircoynl nitrate (containing about 20 mg. of ZrO_2), 5 ml. of 1% ethanolic solution of 3-acetyl-4-hydroxycoumarin was added slowly with constant stirring. A pale yellow precipitate of the zirconyl complex was produced, which was allowed to settle for about 10 minutes in the cold, and after filtration through Whatman filter-paper No. 40, it was washed with water, dried and ignited to ZrO_2. The results obtained are given in Table I.

TABLE I

Weight of ZrO_2 by Oxine method mg.	Weight of ZrO_2 by Coumarin method mg.
2·20	2·20
10·25	10·30
19·75	19·75
50·00	49·75
99·75	100·00

Effect of pH on the formation of the zirconyl complex.—The effect of pH on the formation of the complex was studied by buffering the zirconyl salt with ammonium acetate for higher pH values (above pH 3·0) and by adding 0·1 N HC for lower pH values (below pH 3·0). The determination of zirconium can conveniently be carried out within quite a broad pH range (pH 3·5 to 7·0) as can be seen from Table II.

TABLE II

pH	Weight of ZrO_2 taken mg.	Weight of ZrO_2 found mg.
2·00	19·75	2·15
2·50	19·75	4·80
3·00	19·75	19·00
3·50	19·75	19·75
4·00	19·75	19·75
5·00	99·75	100·00
6·00	50·00	49·75
7·00	19·75	19·70

Determination of titanium with 3-acetyl-4-hydroxycoumarin.—To an aliquot portion of potassium titanyl oxalate solution (containing about 15 mg. of TiO_2), 10 ml. of 1% ethanolic solution of 3-acetyl-4-hydroxycoumarin was added slowly with constant stirring. About 5 gm. of ammonium acetate was then added to it. The resultant solution containing the pale yellow precipitate so produced was warmed on a water-bath for about 15 minutes. It was then cooled to room temperature, filtered through Whatman filter paper No. 40, washed with water, and after drying ignited to TiO_2.

The results obtained are given in Table III.

TABLE III

Weight of TiO_2 by Oxine method mg.	Weight of TiO_2 by Coumarin method mg.
7·10	7·10
13·65	13·70
27·50	27·55
34·45	34·40
67·00	67·20

Effect of pH on the precipitation of titanium with 3-acetyl-4-hydroxycoumarin.—The effect of pH on the precipitation of titanium using the above reagent was studied. From pH 2·8 to 4·5, it was found that the precipitate of the titanium complex formed was colloidal in nature and could be filtered to give a clear filtrate only in presence of a little ammonium chloride. A 10% solution of ammonium acetate was used for raising the pH of the complex up to 7, and ammonium acetate-ammonium hydroxide mixture was used for raising the pH of the complex from 7·0 to 8·0. Table IV shows the results obtained.

TABLE IV

Wt. of TiO_2 taken (Oxine method) = 13·65 mg.

pH	2·8	3·5	4·5	5·5	6·0	7·0	8·0	9·0
Weight of TiO_2 obtained in mg. (Coumarin method) ..	2·50	3·20	6·00	11·80	12·25	13·65	13·60	13·70

SUMMARY

3-Acetyl-4-hydroxycoumarin has been used for the gravimetric determination of zirconium and titanium. This reagent precipitates zirconium quantitatively between pH 3·5 and 7·0, and titanium between pH 7·0 and 9·0.

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THE RAMAN SPECTRA OF ORGANIC COMPOUNDS

Part I. Methyl, Ethyl, *n*-Propyl and *n*-Butyl Alcohols

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1. Introduction

The technique of excitation of Raman spectra by the λ 2537 radiation from a water-cooled mercury are has been widely used in the case of crystals both in this laboratory and elsewhere and many interesting results have been obtained. The application of this method to the case of liquids is, however, beset with some practical difficulties, the most important one being that many liquids are not transparent to the λ 2537 radiation. In spite of these limitations, Bolla (1934) and Narayanaswamy (1947) employed this technique for investigating the Raman spectra of water, methyl and ethyl alcohols and a couple of hydrocarbons. The spectrograms obtained by Narayanaswamy were partly masked by the presence of a strong fluorescence extending from about λ 2600 to λ 2800 A.U. due to the fused silica Raman tube. In recent years better quality fused silica tubes are available, which do not exhibit any fluorescence in this region. Using such good quality fused silica Wood's tube a systematic investigation of the Raman spectra of liquids, which are transparent to the ultra-violet has been undertaken by the author. As expected, considerably improved and new results were obtained in the case of the first four members of normal aliphatic alcohols, and these results are presented in this paper.

2. Earlier Work

Methyl alcohol is one of the substances, the Raman spectrum of which has been studied by many investigators. A complete bibliography on this subject has been given by Narayanaswamy (1947), and also by Halverson (1947). It will not be repeated here. Besides the 'wing', Narayanaswamy reported the existence of 15 Raman lines.

The Raman spectrum of ethyl alcohol has also been the subject of extensive study. A complete bibliography on the Raman spectrum of ethyl alcohol is given by Narayanaswamy (1947). Bolla recorded nearly 56 Raman lines in the spectrum of methyl alcohol, while Narayanaswamy reported the existence of only 31 Raman lines.

The Raman spectra of *n*-propyl and *n*-butyl alcohols were studied by Ganesan and Venkateswaran (1929), Venkateswaran and Bhagavantam (1930), Wood and Collins (1932), Nevgi and Jatkar (1934) and Medard (1934). Trumpy (1930) investigated the Raman spectrum of *n*-propanol and Kohlrausch and Koppl (1935) and Sanyal (1950) investigated the Raman spectrum of *n*-butyl alcohol. Quinan and Weberley (1954) recorded the Raman spectra of all the four alcohols, along with their monodeuterated analogues. The maximum number of Raman lines recorded so far for *n*-propanol was 18 and that for *n*-butanol was 27.

3. EXPERIMENTAL DETAILS

The methyl alcohol used in the present study was of Merck's guaranteed analytical reagent quality. The liquid was distilled twice before being transferred to the Wood's tube. Ethyl alcohol was prepared from commercial sample as follows: The commercial alcohol was repeatedly distilled, then refluxed with a small quantity of H_2SO_4 and distilled again. Next, it was refluxed with pure NaOH (Merck) and distilled. Finally, it was refluxed with CaO and distilled. The final liquid was found to absorb only below 2000 A.U. indicative of the high purity of the sample. *n*-Propyl and *n*-butyl alcohols were B.D.H. 'Analar' samples and were distilled over NaOH before use to remove the traces of aldehydes present. Refractive index and specific gravity measurements indicated that the compounds were very pure.

The intense mercury resonance radiation from a water-cooled and magnet-controlled quartz arc was allowed to fall on the liquid, which was contained in a fused silica Wood's tube. The scattered radiation was condensed on to the slit of a Hilger medium quartz spectrograph. Using a slit width of about 0·04 mm., intense spectrograms were obtained in about 20 to 50 hours with Ilford Zenith Astronomical plates. Using the same plates and a slit width of 0·065 mm. intense spectrograms were obtained with about seven days' exposure with a Hilger E–1 quartz spectrograph. In the case of *n*-propyl alcohol intense pictures could not be obtained because it got decomposed due to prolonged exposure to ultra-violet radiation. The frequency shifts of the Raman lines were evaluated with the help of an iron are comparison spectrum.

3. RESULTS

The Raman spectra of methyl, ethyl, *n*-propyl and *n*-butyl alcohols taken with the Hilger medium quartz spectrograph are reproduced in Figs. 1 (*a*), 1 (*b*), 1 (*c*) and 1 (*d*) respectively, on Plate IV. The frequency shifts of the stronger lines, as well as some of the intense mercury lines are given in the figures. In Fig. 2 (*a*), on Plate V, is reproduced a heavily exposed Raman spectrum of methyl alcohol taken with the E–1 quartz spectrograph,

while Fig. 2 (*b*) exhibits a heavily exposed spectrum of ethyl alcohol taken with the medium instrument. The high frequency shift Raman lines are also marked on the figures. The microphotometer records of the spectra of the four alcohols taken with the medium instrument are reproduced in Figs. 3 (*a*), 3 (*b*), 4 (*a*) and 4 (*b*) respectively, on Plate VI. The frequency shifts together with visual estimates of intensities are given in Tables I–IV.

TABLE I

Raman spectrum of methyl alcohol

Author	Narayana-swamy	Plyler (I.R.)	Assignment
Wing 67	67	..	..
Wing 130	146	..	..
Wing 250	234	..	..
484 (2)	491	..	..
523 (1)	..	..	..
574 (1)	..	..	..
670 (4 *b*)	..	..	ν'_8-OH out-of-place bending
864 (3)	872 (3)	..	..
881 (1)	..	..	..
908 (1)	..	..	..
920 (3)	922 (3)	946	..
1025 (15)	1032 (5)	1033	ν_5 C–O stretching
1109 (8)	1109 (4)	1106	ν'_6 CH_3 rocking
1159 (8)	1150 (3)	1164	ν_9 CH_3 rocking
1200 (1)	..	1213	..
1271 (1)	..	1256	..
1300 to 1430 (6 *b*)	1370 (2 *b*)	1346	ν_8 OH in plane deformation ν'_4-CH_3 asymmetric bending

TABLE I (*Contd.*)

Author	Narayana-swamy	Plyler (I.R.)	Assignment
1450 (16)	1449 (8)	1455 *m*	ν_3-CH_3 symmetric bending
1475 (14)	1470 (7)	1479 *m*	ν_4-CH_3 asymmetric bending
1970 (1)	..	..	$\nu_2 - \nu_5$
2074 (2)	..	2057	$2\nu_5$
2148 (1)	..	..	$\nu_5 + \nu_6'$
2243 (2)		..	$2\nu'_6$
2305 (2)	..	..	$2\nu_6$
2473 (1)	..	..	$\nu_5 + \nu_3$
2551 (6) 2614 (6)	2585 (2 *b*)	..	O–H.....O
2683 (2)	..	2667	O–H.....O
2833 (20)	2833 (10)	2847	$\nu_1, 2\nu_4$
2914 (10)	2911 (5)	2929	ν_2'-CH Asymmetric stretching
2946 (18)	2944 (9)	2946	$\nu_1, 2\nu_4$
2990 (10)	2989 (5)	2989	ν_2-CH Asymmetric stretching
3200 to 3550	3380	..	ν_7 O–H stretching (associated)
3846 (1)	..	..	$\nu_1 + \nu_5$
3934 (2)	..	..	$\nu_1 + \nu_6'$
4044 (4 *b*)	..	..	$\nu_2 + \nu_5$
4165 (2)	..	..	$\nu_2 + \nu_6$
4275 (2)	..	..	$\nu_1 + \nu_3$

TABLE II

Raman Spectrum of ethyl alcohol

Author	Bolla	Plyler (I.R.)	Assignment
Wing 63	..	..	..
Wing 120	..	..	..
Wing 200			
267 (4)	257 (2)	267	ν_{13} CH_3 twisting
359 (1)	..	353	..
432 (10)	433 (6)	427	ν_{12} C–C–O skeletal bending
525 (4)	..	..	..
549 (4)	..	..	..
674 (0)	..	..	ν_{11} OH out-of-plane deformation
775 (6)	..	..	ν_{14} CH_2 rocking
818 (8)	814 (3)	801	..
843 (1)	..	..	2 × C–C–O bending
877 (20 *b*)	883 (60)	877	ν_5 C–C skeletal stretching
935 (4)	..	..	ν_{15} CH_3 out-of-plane wagging
1032 (2)	1032 (1)	..	..
1050 (20 *b*)	1051 (32)	1067	ν_4 C–O skeletal stretching
..	1073 (1)	..	..
1090 (16)	1096 (27)	..	ν_{16} CH_2 twisting
1121 (4)	1125 (6)	..	ν_{17} CH_3 in plane wagging
1163 (2)	1160 (2)	..	..
1276 (10)	1274 (17)	1242	ν_{18} CH_2 wagging
1384 (2)	1386 (5)	1391	ν_{10} OH in plane deformation

TABLE II (*Contd.*)

Author	Bolla	Plyler (I.R.)	Assignment
1417 (2 *b*)	..	..	ν_9 CH bending
..	1445 (1)	..	..
1452 (18 *b*)	1455 (46)	1456	ν_8 CH bending
1485 (15 *b*)	1484 (10)	..	ν_7 CH bending
1620 (2)	1618 (4)	..	2 × C–C stretching
1680 (0 *b*)	..	..	..
..	1885 (0)	..	..
..	1921 (0)	..	..
1974 (1)	1969 (0)	..	$\nu_{16} + \nu_5$
..	2065 (1)	..	
2091 (2)	2093 (1)	2110	$2\ \nu_4$
..	2138 (0)	..	
2183 (1)	2188 (0)	2160	$2\ \nu_{16}$
2250 (2)	2254 (1)	..	$\nu_5 + \nu_{10}$
2283 (2)	2281 (1)	..	$\nu_5 + \nu_9$
2330 (1)	2327 (0)	..	$\nu_8 + \nu_5$
2439 (1)	2431 (1)	..	$\nu_4 + \nu_{10}$
2474 (2)	2476 (1)	..	$\nu_{10} + \nu_{16}$
2547 (4)	2546 (2)	..	O–H.....O
2598 (4)	2597 (2)	..	,,
2654 (2)	2647 (1)	..	,,
2719 (15 *b*)	2717 (7)	..	,,
2755 (10)	2752 (4)	..	,,

TABLE II (*Contd.*)

Author	Bolla	Plyler (I.R.)	Assignment
2829 (16 *b*)	2835 (5)	..	,,
2880 (20)	2879 (59)	2890	ν_3 C–H stretching
2929 (20)	2929 (100)	2924	ν_2 ,,
2976 (20)	2972 (61)	2977	ν_1 C–H stretching
3232 (6 *b*)	3240 (3)	..	,,
3390	3359 (10)	..	ν_6 O–H stretching—associated molecule
3628 (2)	3632 (2)	..	O–H stretching monomer
3662 (1)	3685 (0)	..	$\nu_3 + \nu_{14}$
3839 (2)	3852 (2)	..	$\nu_1 + \nu_5$
3948 (1)	3945 (0)	..	$\nu_3 + \nu_4$
4020 (2)	4053 (2)	..	$\nu_1 + \nu_4$
4092 (1)	..	..	$\nu_1 + \nu_{17}$
4237 (2)	4242 (0)	..	$\nu_1 + \nu_{18}$

TABLE III

Raman spectrum of n-*propyl alcohol*

Author	Wood and Collins	Plyler (I.R.)	Assignment
160 wing	..	..	Wing
240 (0)	..	..	CH_3 twisting
332 (2)	324 (2)	..	Skeletal bending
463 (8)	458 (4)	463 *m*	Skeletal bending
670 (0)	..	..	OH in plane bending

TABLE III (*Cont'd.*)

Author	Wood and Collins	Plyler (I.R.)	Assignment
770 (4)	757 (4)	758 *w*	CH_2 rocking
821 (1)	..	..	..
860 (15)	856 (10)	..	C–C skeletal stretching
882 (12)	..	898 *m*	C–C skeletal stretching
928 (1)	..	..	..
968 (8)	967 (4)	971 *s*	CH_3 out-of-plane wagging
987 (0)	..	..	..
1020 (1)	..	1013 *w*	..
1054 (12)	1049 (5)	1047 *m*	C–O skeletal stretching
1070 (10)	1064 (6)	1066 *v.s.*	..
1101 (10)	1100 (6)	..	CH_2 twisting
1133 (4 *b*)	..	..	CH_3 in plane wagging
1172 (0)	..	..	..
1204 (0)	..	..	..
1237 (4)	..	1218 *s*	CH_2 twisting
1251 (1)	..	..	..
1273 (8)	1268 (4)	1276 *v.w.*	CH_2 wagging
1300 (10)	1296 (6)	..	CH_2 wagging
1342 (2)	..	..	882 + 463
1385 (1)	..	1393 *s*	OH in plane bending
1451 (15)	1451 (10)	..	CH bending
1467 (10 *b*)	..	1464 *m*	CH bending
1501 (0)	..	..	1054 + 463

TABLE III (*Contd.*)

Author	Wood and Collins	Plyler (I.R.)	Assignment
1640 (0)	..	..	1300 + 332
2110 (0)	..	..	1054 × 2
2197 (0)	..	..	1300 + 882
2240 (0)	..	..	1101 + 1133
2338 (0)	..	..	1451 + 882
2460 (0)	..	..	1133 + 1300
2550 (2 *b*)	..	..	O–H.....O
2595 (4)	..	..	,,
2677 (8)	2663 (1)	..	,,
2738 (12)	2731 (2)	..	,,
2876 (20)	2873 (15)	2892 *m*	CH stretching
2915 (18)	2905 (10)	2929 *s*	,,
2942 (18)	2931 (10)	2946 *s*	,,
2970 (18)	2963 (10)	2978 *s*	,,
3232 (4 *b*)	..	..	2915 + 332
3380 (Band max.)	..	..	O–H stretching—associated
3630 (2)	..	..	O–H stretching—monomer
3685 (1)	..	..	2915 + 770

4. DISCUSSION

Methyl alcohol.—Thirty-five Raman lines have been observed in the spectrum of methyl alcohol of which 20 have been recorded for the first time. The frequency shifts observed by Narayanaswamy are given in column 2 of Table I. In the third column are given the positions of prominent infra-red absorption maxima observed by Plyler (1932). The 'wing' accompanying

TABLE IV

Raman spectrum of n-*propyl alcohol*

Author	Wood and Collins	Quinan and Weberley (I.R.)	Assignment
0– 200	..	..	Wing
272 (1)	..	..	CH_3 twisting
349 (5)	350 (2)		
398 (12)	394 (6)	..	C–C–C–C–O skeletal bending
450 (4)	448 (2)		
485 (4)	483 (2)	..	..
515 (4)	514 (2)	..	..
670 (0)	..	698	O–H out-of-plane bending
748 (2)	..	738	CH_2 rocking
807 (8)	805 (4)	799	
825 (15)	825 (8)	..	
844 (6)	845 (3)	853	CH_3 Wagging
882 (8)	877 (4)	..	C–C Stretching
903 (8)	901 (4)	..	
945 (8)	944 (4)	..	
963 (8)	963 (4)	954	
971 (8)	..	..	
992 (1)	..	997	
1025 (8)	1025 (4)	1021	
1057 (8)	1051 (4)	1057	C–O skeletal stretching
1072 (10)	1067 (4)	1070	

TABLE IV (*Contd.*)

Author	Wood and Collins	Quinan and Weberley (I.R.)	Assignment
1110 (10)	1104 (6)	..	CH_2 twisting
1136 (3)	1135 (1)		
1222 (4)	..	1210	
1256 (6)	..	..	CH_2 wagging
1304 (12)	1296 (1)	..	
1343 (1)	..	..	
1369 (1)	..	..	
1382 (1)	..	1394	O–H in plane bending
1433 (15)	..	..	C–H bending
1448 (15)	1447 (10)	..	
1465 (15)	..	..	
1481 (12 *b*)	1476 (4)	..	
1896 (0)	..	..	1072 + 825
2196 (2)	..	..	1304 + 882
2274 (1)	..	..	1448 + 825
2332 (0)	..	..	1448 + 882
2428 (2)	..	..	1304 + 1110
2485 (1)	..	..	1222 + 1256
2523 (1)	..	..	1448 + 1072
2593 (4)	..	..	O–H.....O
2667 (4)	2660 (1)	..	,,
2690 (4)	..	..	,,

TABLE IV (*Contd.*)

Author	Wood and Collins	Quinan and Weberley (I.R.)	Assignment
2720 (8)	..	..	O-H.....O
2744 (8)	2733 (1) ..	..	,,
2871 (20)	2865 (10)	2853	C–H stretching
2906 (20)	2903 (10)	2893 2926	
2938 (20)	2932 (10)	2949	
2965 (20)	2963 (15)	2973	
3221 (6 *b*)	..	..	2965 + 272
3390	..	..	O–H stretching—associated
3640 (2)	..	..	O–H stretching—monomer
3685 (1)	..	3682	2938 + 748

the Rayleigh line is found to extend up to 250 wave numbers. It exhibits two maxima, at about 67 and 130 cm.$^{-1}$ which are in agreement with the values given by Narayanaswamy. Because of the fluorescence of the container, Narayanaswamy was able to record only the very intense lines in the high-frequency shift region. The O–H stretching band extends from about 3200 to 3550 cm.$^{-1}$ with a maximum at about 3370 cm.$^{-1}$ The appearance of a series of weak and broad lines in the region 3800 to 4200 cm.$^{-1}$ is a new feature of the spectrum of methyl alcohol (Fig. 2 *a*).

From theoretical considerations it can be shown that methyl alcohol molecule should exhibit twelve fundamental vibrational frequencies, eight of them (ν_1 to ν_8) symmetric with respect to the C–O–H plane, and four (ν_2', ν_4', ν_6' and ν_8') antisymmetric with respect to the above plane. Frequencies of the first three antisymmetric vibrations may be expected to lie close to those of three symmetric vibrations.

All the twelve frequencies should be present in the Raman spectrum of methyl alcohol. They have been identified and their assignments are

indicated in column 4 of Table I. As frequency shift of the overtone of ν_4, *i.e.*, $2\nu_4$ is nearly equal to that of ν_1, one should expect Fermi resonance splitting. The two Raman lines arising therefrom are 2833 and 2946 cm.$^{-1}$ They have been assigned as ν_1 and $2\nu_4$.

The assignments given in Table I are in general agreement with those given by Margottin-Maclou (1960) for methyl alcohol vapour. One CH_3 rocking frequency at about 1070 cm.$^{-1}$ in the vapour might have shifted to 1109 cm.$^{-1}$ in the liquid due to association. The existence of two Raman lines at 1056 and 1171 cm.$^{-1}$ observed by Halford, Anderson and Kissin (1937) in the spectrum of methyl alcohol has not been confirmed and hence assignments given by Herzberg (1945) based on these Raman lines may have to be revised.

The comparatively fainter lines appearing in the region 1900–2500 cm.$^{-1}$ and 3800–4300 cm.$^{-1}$ have been explained as combinations and the respective assignments have been indicated in Table I. The Raman line at about 1970 cm.$^{-1}$ may be assigned as a differential, *i.e.*, $\nu_2-\nu_5$ and the corresponding summational appears with moderate intensity at 4044 cm.$^{-1}$

There are 3 Raman lines between 2500 and 2800 cm.$^{-1}$, two of which are too intense to be explained as summation frequencies, and the third at 2683 cm.$^{-1}$ does not seem to correspond to any summational frequency. These lines are assigned to the O–H.....O vibrations, due to hydrogen bonding between the hydroxyl groups of associated methyl alcohol molecules in the liquid state.

Van Thiel *et al.* (1957) have shown that methyl alcohol can form cyclic and open-chain dimers and higher polymers. The maxima observed in the 'wing' at about 67 and 130 cm.$^{-1}$ might correspond to the rotational oscillations of the CH_3OH units in the dimers and polymers about the hydrogen bond.

There are quite a few weak Raman lines, namely, 484, 523, 574, 964, 881, 908, 920, 1200 and 1271 cm.$^{-1}$, which could not have been assigned either to any of the fundamental vibrations of the CH_3OH molecule or to their differentials. They may have to be attributed to the internal oscillations modified under the influence of association.

Ethyl alcohol.—Forty-nine Raman lines have been recorded for this liquid (Table II). The frequency shifts reported by Bolla are given in column 2. Though Narayanaswamy (1947) was able to record a few faint lines below 1000 cm.$^{-1}$ many of the fainter lines in the region 2000–4500 cm.$^{-1}$ were not recorded by him. The author was unable to confirm the existence

of some of the fainter lines reported by Bolla. The prominent infra-red absorption maxima reported by Plyler (1952) are given in column 3. The O–H band extends from 3200–3550 cm.$^{-1}$ exhibiting two maxima at about 3232 and 3390 cm.$^{-1}$ The 'wing' in ethyl alcohol extends up to 200 cm.$^{-1}$ and exhibits two maxima at about 63 and 120 cm.$^{-1}$

The C_2H_5OH molecule should possess 21 fundamental modes of vibration, all of which are expected to appear in the Raman effect. The assignments of the observed Raman lines to the vibrational frequencies marked arbitrarily as ν_1 to ν_{18} are indicated in column 4 of Table II. These are done by comparing the observed intensities of the Raman lines and making use of the infra-red data of Plyler (1952), and Barrow (1952) on ethyl alcohol and Sheppard (1949) on ethyl halides.

As in the case of methyl alcohol, the fainter lines between 1900–2500 cm.$^{-1}$ and 3800–4300 cm.$^{-1}$ are assigned to combination frequencies, and the stronger lines between 2500 and 2800 cm.$^{-1}$ to O–H.....O vibrations. The 'wing' structure could once again be attributed to the rotatory oscillations of the C_2H_5OH units in the associated groups about the hydrogen bond.

An interesting feature of the Raman spectrum of ethyl alcohol is the presence of two lines in the region of the free O–H stretching vibration, *i.e.*, 3600–3700 cm.$^{-1}$ The higher frequency line at 3662 cm.$^{-1}$ is the weaker of the two, and can be attributed to a combination frequency. Then the stronger line at 3628 cm.$^{-1}$ can be explained as due to the O–H stretching vibration of the single or unassociated molecule.

In this case also, there are a few faint lines of low-frequency shifts, which correspond neither to the fundamental vibrations of the molecule nor to combinations. These lines might owe their origin to the internal oscillations of the associated molecule. The fairly intense line at 818 cm.$^{-1}$ may be ascribed to the C–C skeletal stretching oscillations the frequency of which has been lowered due to association.

n-*Propyl alcohol.*—As mentioned earlier, the spectrum of this compound is very weak because of the fact that the sample got decomposed due to over-exposure. Forty-five Raman lines have been recorded and are given in Table III. The frequency shifts reported by Wood and Collins (1932) are given in column 2. About 27 Raman lines have been recorded for the first time. The infra-red data of Plyler (1952) are given in column 3. The 'wing' accompanying the Rayleigh line is very faint and extends up to 160 cm.$^{-1}$ and does not seem to show any maximum. The O–H band in this case extends from about 3200–3500 cm.$^{-1}$ exhibiting two maxima at about 3232 and 3380 cm.$^{-1}$ The important Raman lines have been assigned

to the fundamental modes of vibration of the *n*-propyl alcohol molecule as indicated in column 4 of Table III. Simpson and Sheppard (1955) have shown that the skeletal frequencies of alcohols and amines can be identified by comparison with the corresponding fluoride or the next higher hydrocarbon in the series. Thus, considering *n*-propyl alcohol molecule, it is seen that it has approximately the same molecular weight and contains the same number of CH_2 groups as *n*-butane–$CH_3CH_2 \cdot CH_2 \cdot CH_3$. Hence, by a judicious comparison of the data concerning this molecule, the fundamental vibrational frequencies of *n*-propyl alcohol can be identified with reasonable accuracy. But *n*-butane is known to exist as a mixture of rotational isomers in the liquid state. This difficulty is overcome by using the data for only one form of *n*-butane, in this case, trans-*n*-butane. The vibrational analysis for the latter molecule has been made by Szasz, Sheppard and Simpson (1948), and these are used in assigning the fundamental frequencies of *n*-propyl alcohol.

The fainter Raman lines appearing in the region 2000–2500 cm.$^{-1}$ are explained as combinations and those between 2500 and 2800 cm.$^{-1}$ as due to O–H.....O vibrations. As in the case of ethyl alcohol, here also there are two lines in the region 3600–3700 cm.$^{-1}$ The stronger of the two, *i.e.*, 3630 cm.$^{-1}$ is assigned to the O–H stretching vibration of the unassociated molecule and the other fainter line at 3685 cm.$^{-1}$ is explained as a combination frequency.

n-*Butyl alcohol.*—Fifty-one Raman lines have been recorded in the spectrum of *n*-butyl alcohol and are given in column 1 of Table IV. 24 of them are recorded for the first time. In columns 2 and 3 are given the frequency shifts reported by Wood and Collins (1932) and infra-red absorption maxima reported by Quinan and Weberley (1959) respectively. The O–H band extends from 3200–3550 cm.$^{-1}$ exhibiting two maxima at about 3221 and 3390 cm.$^{-1}$ There is a weak fluorescence superposed on this band. The 'wing' accompanying the Rayleigh line extends up to about 200 cm.$^{-1}$ and does not seem to show any structure.

The assignments of the important Raman lines observed are indicated in column 4 of Table IV. These are made by an extension of the assignments for *n*-propyl alcohol, and also by comparing the results obtained for *n*-butyl alcohol, with those of *n*-pentane. For the above purpose, only the data on the gauche form of *n*-pentane given by Tchamler (1954) are used.

There are a series of 8 sharp and intense Raman lines with the frequency shifts varying from 807 cm.$^{-1}$ to 971 cm.$^{-1}$. The CH_2 rocking, C–C and CH_3 wagging modes of oscillations are expected to give intense Raman lines

in this region. There should be three different types of C–C oscillations in the butyl alcohol giving rise to three different Raman lines. One might expect further splitting of some of these modes due to the existence of the phenomenon of rotational isomerism (Berthelot, 1950 and Brown, Simpson and Sheppard, 1950). In view of the larger number of lines of nearly equal intensity appearing in this region, it is difficult to assign a particular Raman line to a particular mode. They have therefore been clubbed together in Table IV.

The faint lines appearing in the region 1850-2000 cm.$^{-1}$ have been assigned as combinations and those between 2500 and 2800 cm.$^{-1}$ as O–H.....O frequencies. In this spectrum also there are two Raman lines between 3600 and 3700 cm.$^{-1}$, the lower frequency one being assigned as the O–H stretching frequency of the single molecule and the higher frequency one as a combination.

SUMMARY

The Raman spectra of methyl alcohol, ethyl alcohol, *n*-propyl alcohol and *n*-butyl alcohol have been recorded using λ 2537 excitation. 35, 49, 45 and 51 Raman lines respectively have been identified in the spectra of these alcohols, in addition to the rotational 'wings'. In each case, a large number of additional lines have been recorded. The existence of Raman lines with frequency shifts greater than 3800 cm.$^{-1}$, first reported by Bolla in the spectrum of ethyl alcohol, has been confirmed. Similar high-frequency shift Raman lines have also been recorded in the spectrum of methyl alcohol. They have been assigned as combinations. Proper assignments have been given for the prominent Raman lines appearing in the spectra of these alcohols.

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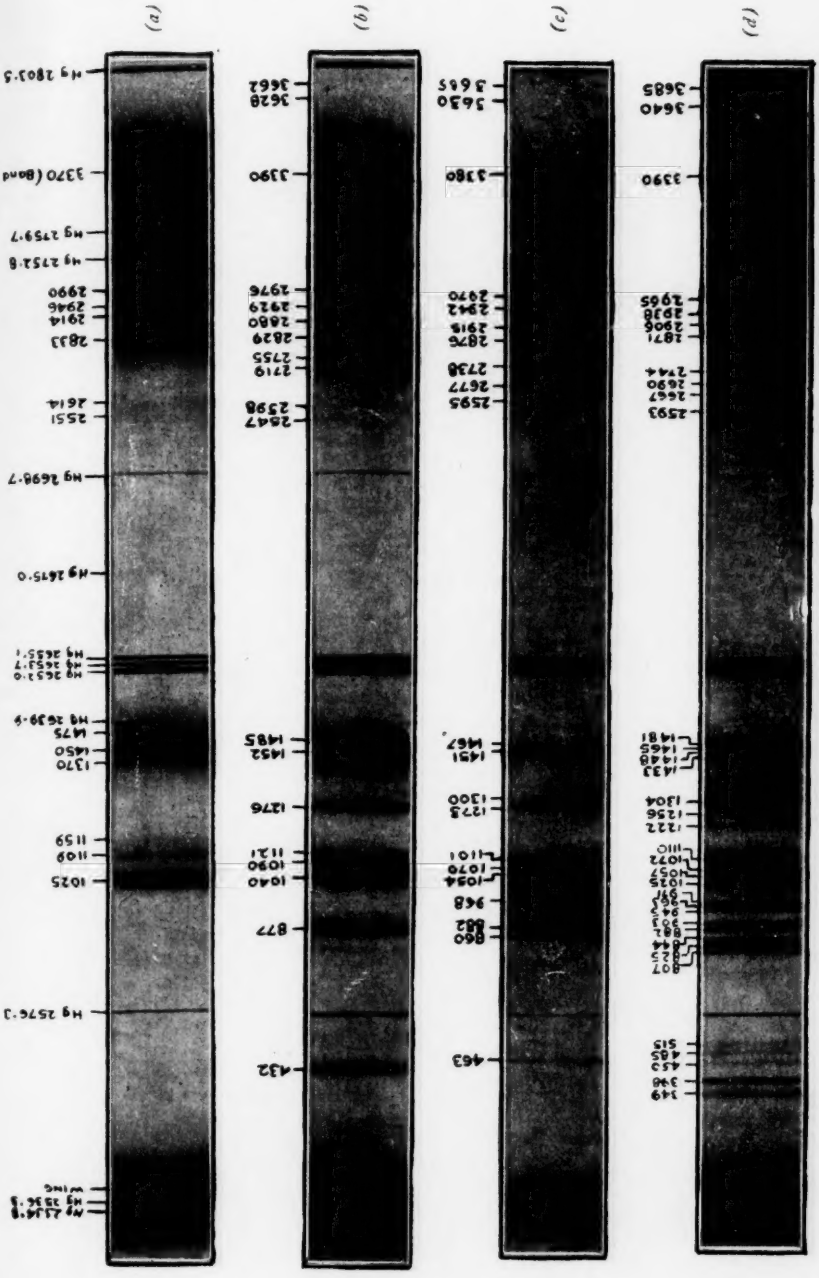


FIG. 1. (*a*) Raman spectrum of methyl alcohol taken with E-3 spectrograph.
(*b*) ,, ethyl ,, ,,
(*c*) ,, *n*-propyl ,, ,,
(*d*) ,, *n*-butyl ,, ,,

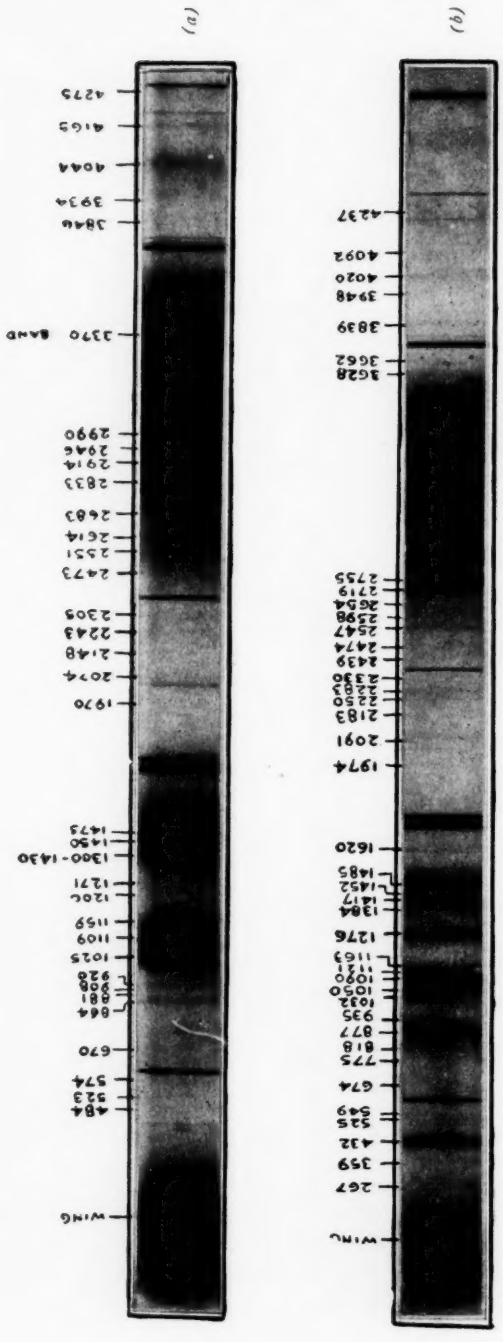
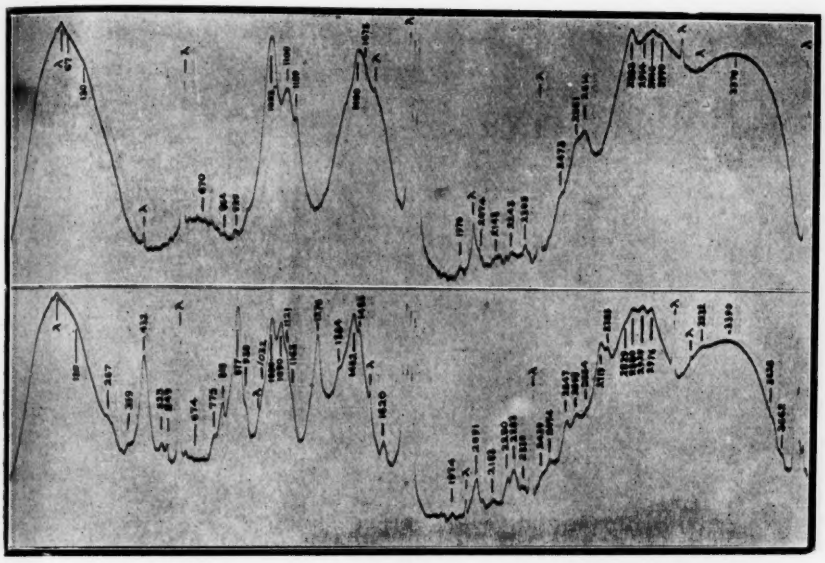


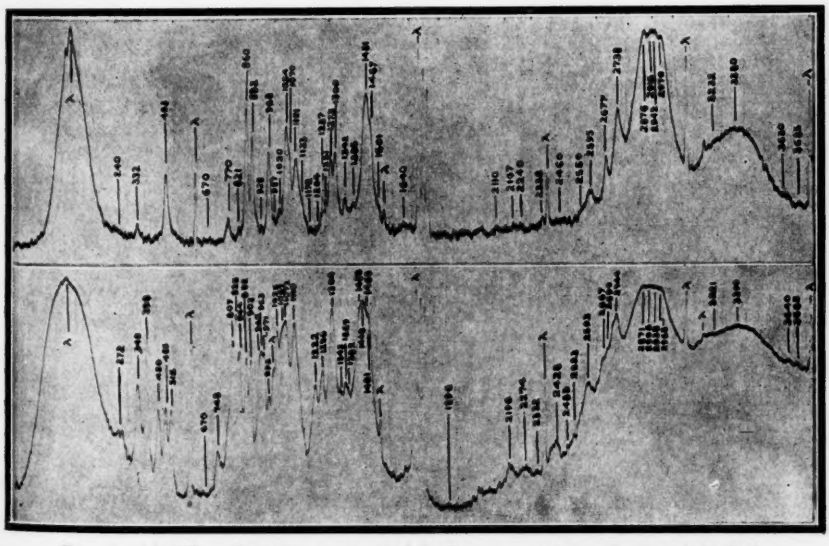
FIG. 2. (*a*) Raman spectrum of methyl alcohol taken with E-1 spectrograph.
(*b*) Heavily exposed Raman spectrum of ethyl alcohol taken with E-3 spectrograph.



(a)

(b)

FIG. 3. (a) Microphotometer record of the Raman spectrum of methyl alcohol.
(b) ,, ,, ,, ethyl alcohol.



(a)

(b)

FIG. 4. (a) Microphotometer record of the Raman spectrum of *n*-propyl alcohol.
(b) ,, ,, ,, *n*-butyl alcohol.

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